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# Molecular limits to the quantum confinement model in diamond clusters

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The electronic structure of monodisperse, hydrogen-passivated diamond clusters in the gas phase has been studied with x-ray absorption spectroscopy. The data show that the bulk-related unoccupied states do not exhibit any quantum confinement. Additionally, density of states below the bulk absorption edge appears, consisting of features correlated to CH and CH<sub>2</sub> hydrogen surface termination, resulting in an effective red shift of the lowest unoccupied states. The results contradict the commonly used and very successful quantum confinement model for semiconductors which predicts increasing band edge blue shifts with decreasing particle size. Our findings indicate that in the ultimate size limit for nanocrystals a more molecular description is necessary.

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Quantum confinement is a very successful model for understanding the electronic structure of nanometer size semiconductor structures such as quantum wells, nanocrystals and clusters. Generally speaking it predicts that with decreasing particle sizes the bandgap increases due to shifting of the band edges. So far, experiments were typically performed on deposited or embedded systems comprised of at least several tens or hundreds of atoms. Now, with the isolation of diamondoids [1] a new class of clusters allows a study of quantum confinement in the molecular size limit. The first diamondoid, adamantane, consists of the smallest possible single cage unit excised from the diamond lattice, with the dangling bonds terminated by hydrogen atoms. Each subsequent diamondoid adds one additional face-fused cage. From a basic sciences point of view the isolated diamondoids are perfectly size-selected and hydrogen terminated diamond (group IV semiconductor) clusters in the bulk crystal lattice configuration. This class of ideal structures has been the basis for virtually all electronic structure calculations on semiconductor nanocrystals. To date, however, these perfect nanometer-sized structures have never been available and thus have not been investigated. Experimental systems researched thus far exhibit either a size distribution or are charged for mass separation, possess ill-defined surface reconstruction or termination, and are typically deposited on substrates inducing interaction with their environment while under investigation.

Diamond plays a special role within the group IV semiconductors. Experimentally, deposited Si [2] and Ge [3] nanocrystals with sizes above 1 nm exhibit clear, theoretically confirmed quantum confinement effects. Meanwhile, reports show large and controversial quantum confinement effects for CVD grown nanocrystalline diamond[4–6], yet no confinement is measured for 4 nm nanodiamond[7]. Theoretically diamond nanocrystals have been predicted to exhibit significant quantum confinement effects for sizes below 1 nm with the HOMO-LUMO gap to increase up to 7.6 eV [7–9], while the bulk diamond bandgap is 5.47 eV[9].

In this letter we report x-ray absorption (XAS) measure-

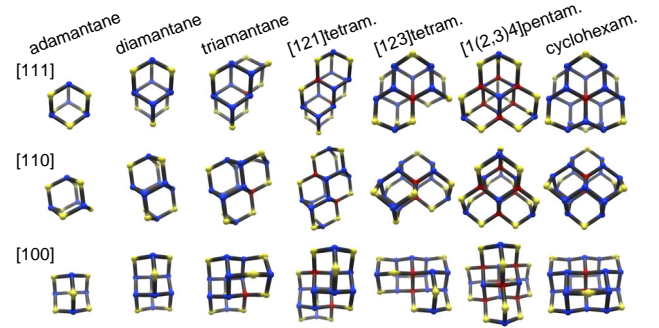


FIG. 1: Diamondoids investigated from adamantane to cyclohexamantane are shown in columns. The three rows presented view the diamondoids along various corresponding bulk lattice vectors. Colors indicate bulk-coordinated, CH, and CH<sub>2</sub> with red, blue, and yellow respectively.

ments on diamondoids in the gas phase ranging from adamantane (one diamond cage) to cyclohexamantane (six diamond cages) as pictured in Fig. 1. Synchrotron-based XAS is ideal for determining electronic structure and bonding configuration in carbon materials [10]. Measurements in the gas phase allow experimental investigation of the ideal, interaction-free systems forming the basis for the theoretical models. To the best of our knowledge, the current experimental results in the molecular limit of ideal semiconductor nanocrystals yield unprecedented data against which competing theoretical models can be tested.

The diamondoids are extracted from petroleum and size separated by high-performance liquid chromatography in ultra-high purity [1]. Fig. 1 shows structures of the investigated diamondoids adamantane, diamantane, triamantane, [121] tetramantane, [123] tetramantane, [1(2,3)4] pentamantane and cyclohexamantane (using Balaban-Schleyer structural nomenclature[11]). The diamondoids are perfectly size-selected, neutral, are fully sp<sup>3</sup> hybridized, and exhibit a complete hydrogen surface termination. This surface is of particu-

TABLE I: Carbon binding environments in each diamondoid.

	chem. formula	bulk C	surface CH	CH <sub>2</sub>
adamantane	C <sub>10</sub> H <sub>16</sub>	0	4	6
diamantane	C <sub>14</sub> H <sub>20</sub>	0	8	6
triamantane	C <sub>18</sub> H <sub>24</sub>	1	10	7
[121] tetramantane	C <sub>22</sub> H <sub>28</sub>	2	12	8
[123] tetramantane	C <sub>22</sub> H <sub>28</sub>	2	12	8
[1(2,3)4] pentamantane	C <sub>26</sub> H <sub>32</sub>	6	8	12
cyclohexamantane	C <sub>26</sub> H <sub>30</sub>	2	18	6

lar interest as such a hydrogen termination is used in most theoretical models describing semiconductor nanoclusters. Table I summarizes the stoichiometric formulas and atomic environments of the various diamond clusters. Only three basic configurations exist: carbon bound to only other carbon atoms (C), carbon bound to three other carbon atoms and one hydrogen (CH), and carbon bound to two carbon and two hydrogen atoms (CH<sub>2</sub>). In a bulk diamond picture, atoms (C) can be interpreted as bulk-coordinated whereas the atoms bound to hydrogen (CH and CH<sub>2</sub>) can be considered surface atoms.

Fundamental geometric properties of investigated clusters can be inferred from Fig. 1 and table I. The most basic diamondoids adamantane and diamantane only exhibit surface carbon atoms. Triamantane exhibits the first fully bulk-coordinated atom. Both isomers of tetramantane are stoichiometrically similar but [121] tetramantane exhibits a straight geometry while the [123] isomers, with left- and right-helicity, have a bent geometry. Pentamantane, a compact, tetrahedral structure, has a significant higher fraction of bulk coordinated atoms than cyclohexamantane which exhibits a disc-like structure.

The x-ray absorption measurements were performed at the high-resolution undulator beamline BW3 at the Hamburger Synchrotronstrahlungslabor HASYLAB at the Deutsches Elektronensynchrotron DESY in Hamburg (Germany). In brief, a monochromatized photon beam is crossed with the cluster beam under the aperture of a time-of-flight spectrometer (TOF). The diamondoids are brought into the gas phase by sublimation at room temperature or by gentle heating up to 200° C with a temperature-stabilized in-vacuum furnace. The cluster beam is guided to the interaction region with a heated nozzle to avoid recondensation and no carrier gas is used. For measuring the XAS spectra the photon energies are scanned through the C1s absorption edge. From direct or auto ionization as well as core hole decay processes the clusters are charged and all ionic fragments are detected with the TOF. The recorded total ion yield approximates the absorption cross section and from the spectra conclusions about the atomic environment and electronic structure of the excited atom can be drawn.[10] The final state of the XAS process includes a core hole localized at the excited atom. It's influence will shift the energy levels on an absolute scale by multiple eV compared to ground state energies. However, as the core hole effect is similar for all diamondoids it does not affect trends and

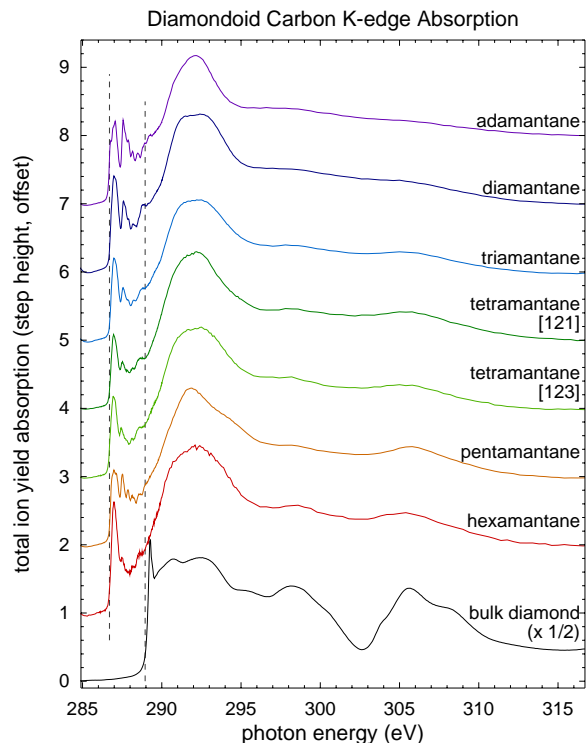


FIG. 2: The Carbon K-edge absorption of the diamondoids adamantane to hexamantane, and a bulk diamond reference.

relative comparisons in a series of diamond clusters. Highly oriented pyrolytic graphite (HOPG) C K-edge absorption was measured with the transmitted beam to calibrate energy scales. The beamline resolution was determined to be better than 0.1 eV. All spectra were normalized to the photon flux, measured with a highly transmissive Au grid. Pressures while acquiring the data were on the order of  $10^{-6}$  mbar and the base pressure of the detector chamber was  $10^{-8}$  mbar with partial pressures related to carbon contamination being in the  $10^{-11}$  mbar regime. Characterization of the adamantane beam with mass spectrometry showed only single molecules and no larger aggregates.

Fig. 2 presents the C K-edge absorption data for the diamond cluster series from adamantane to cyclohexamantane and a diamond crystal reference. The spectra of the smallest diamondoids resemble previous XAS of the closely related cyclohexane [12] and earlier electron energy loss spectra (EELS) of gas-phase adamantane [13]. Through the series to larger sizes, though, the spectra already begin to exhibit the basic band structure of bulk diamond as the second absolute gap at 303 eV emerges [14]. The diamondoids exhibit sharp spectral features starting at 286.7 eV, about 2.3 eV below the absorption onset of the diamond reference sample. This spectral intensity is in the energy range of Rydberg, C-H valence, and mixed Rydberg-valence states of gaseous hydrocarbon molecules [10, 12]. Furthermore, the features are comparable in energy to the intramolecular excitation within the C-H

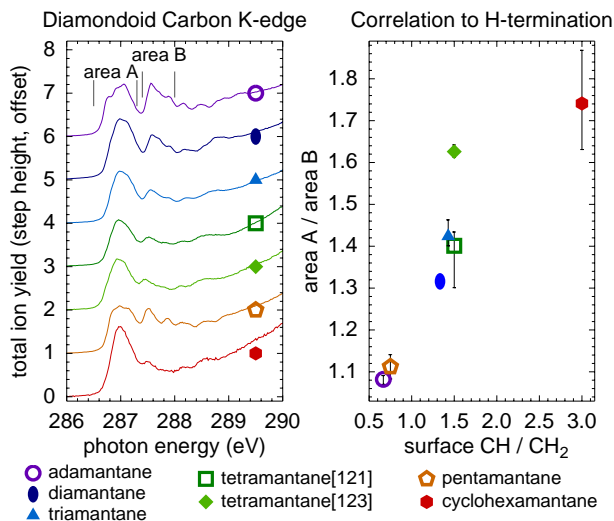


FIG. 3: Pre-edge Carbon K-edge absorption spectra for the diamondoids adamantane to hexamantane (left) and empirical correlation between the manifolds labeled "A" and "B" with the two different surface species CH and CH<sub>2</sub> (right).

bond of hydrogen terminated diamond (111) and (100) surfaces [15, 16]. The left hand panel of Fig. 3 presents the near edge structure from 286 to 290 eV in more detail. The absorption onset is essentially the same for all clusters at 286.7 eV. Two manifolds of peaks, with an abundance of fine structure, and separated by a gap at 287.4 eV, are labeled "area A" and "area B". Resolvable peak positions within these manifolds have energy spacings of 140 - 170 or 340 - 390 meV, and such modulation can be attributed to vibrational structure of the resonances [17]. The observed energy spacings are similar to CH / CH<sub>2</sub> stretches and CH bending modes for condensed diamondoids determined by Raman and infrared absorption [18, 19], and for hydrogenated diamond surfaces with high-resolution EELS [20]. Therefore the measured pre-edge features are attributed to be primarily of CH valence character with clear vibrational structure and thus can be considered "surface states" of the diamond clusters. An empirical correlation between the features labeled area A and B in the left hand panel of Fig. 3 can be made with the number of CH to CH<sub>2</sub> terminations (table I) on each molecule. The right hand panel of Fig. 3 presents the intensity of area A divided by area B, vs. the number of CH divided by CH<sub>2</sub> terminations. A nearly direct linear dependence occurs between the two; therefore area A is primarily due to CH valence states, while area B is dominated by CH<sub>2</sub> valence orbitals. It is interesting to note that [123] tetramantane deviates from this line, and has an intensity which more closely resembles that of cyclohexamantane (see Fig. 1). This effect may be due to geometrical effects on these molecular orbitals, as these two diamondoids are very similar in shape. Additionally, steric hindrance of the additional CH<sub>2</sub> terminations in the [123] tetramantane can also contribute to this effect.

Following the absorption edge in Fig. 2 towards higher

photon energies, just beyond the bulk absorption onset, the pre-edge features merge into a broad resonance centered at 292 eV. These density of unoccupied states (*udos*) can be attributed to the  $\sigma^*$  states of the C-C bonds in a molecular picture [10, 12]. It is these interior  $\sigma^*$  states in the diamondoids (Fig. 2) which evolve through nanodiamond [7] to the bulk crystal (Fig. 2) where they constitute the first band including the conduction band minimum. For ease of reference, the C-C bond related states will therefore be referred to as bulk related *udos* while the CH and CH<sub>2</sub> related pre-edge features will be referred to as surface related *udos*. In previous studies on size dependent electronic structure effects in semiconductor nanocrystals (e.g. experimental [2, 3], theoretical [8, 9]) the bulk related states exhibit the quantum confinement effects. While the  $\sigma^*$  resonance slightly changes shape in the transition from adamantane to cyclohexamantane with clear outliers of the compact adamantane and pentamantane structures, no clear blue shift of the lowest bulk related empty states can be identified using the standard routines of extrapolation of the edge features to the baseline [2, 3] or fitting the absorption onset. This finding is independent of the cluster size or the number of bulk coordinated atoms (compare Table I). The experimental results, namely the non-shifted absorption edge and surface related pre-edge features dominating the LUMO, contradict the current understanding of quantum confinement, predicting blue shifted band edges with decreasing size down to the molecular limit.

The observed non-shifted absorption edge is further evidence for the special role of diamond within the group IV semiconductors. In earlier XAS investigations diamond nanocrystals 4 nm in size have no conduction band minimum shift [7], and theoretical predictions show clear quantum confinement only below 1 nm [7-9]. In comparison, the conduction band minima of Si and Ge nanocrystals of 1.2 nm in size were measured with XAS to shift by 0.4 [2] and 1.2 eV [3], respectively, due to quantum confinement effects. Various calculations for small diamond cluster show the band gap to increase up to 7.6 eV [7-9] compared to 5.47 eV of the bulk crystal. The calculated band gap increase coupled with the observed non-shifted bulk related absorption edge indicate that any quantum confinement effects in diamond must solely take place in the valence band, which will be investigated in a future work. Detailed calculations on the ground state electronic structure of the smallest diamondoids [9] predict increasing HOMO-LUMO gaps with decreasing size, i.e., gaps of 6.2, 6.8, 7.2, and 7.6 eV for decamantane, tetramantane, diamantane, and adamantane. The calculations show LUMO shifts up to 4 eV between adamantane and decamantane and 1 eV between adamantane and diamantane or 2 eV and more between adamantane and tetramantane, respectively [9]. Such a shift would be very obvious in the absorption spectra (Fig. 2) but cannot be observed. It should be noted that the calculations do not unambiguously identify if surface or bulk species constitute the LUMO. In any case the predicted shifts are in contrast to our experimental results, namely the non-shifted bulk-related absorption edge and additional surface re-

lated pre-edge features. A recent tight binding calculation [8] for larger clusters predicts no LUMO shift down to 34 carbon atoms which is in good agreement with the bulk related absorption edge of our largest investigated clusters (26 atoms). However, this and all other theoretical approaches [7–9] fail to predict the observed additional spectral features below the bulk absorption onset due to the hydrogen surface. These specific states, effectively reducing the overall particle gap, are fixed in energy and agree energetically with the hydrogen bonds of cyclohexane [12] in the molecular and diamond surface states [15, 16] in the solid state limit. The present experiments show that the hydrogen surface atoms have a significant impact on the overall electronic structure of the diamond clusters to a degree where they dominate the absorption onset and thus lowest unoccupied states.

In summary we have measured the x-ray absorption of perfect, free, and neutral diamond clusters ranging in size from adamantane to cyclohexamantane to gain insight into size dependent changes in the unoccupied states and the evolution of these states into the conduction band structure of diamond. Contradictory to other group IV semiconductors the bulk related absorption onset does not exhibit a size dependent blue shift as expected within the quantum confinement model. Furthermore the diamond clusters exhibit additional spectral intensity below the bulk absorption onset and within the band gap of bulk diamond which can be empirically correlated to the CH and CH<sub>2</sub> species of the surface termination. These states, dominating the absorption onset, have not been appropriately predicted in any of the current theoretical models. The experimental results show that these diamond clusters differ significantly from their related bulk diamond crystal and therefore require a more molecular description in their ultimate size limit.

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